Magnetism and spin dynamics in the cluster compound $[Cr_4S(O_2CCH_3)_8(H_2O)_4](NO_3)_2 \cdot H_2O$

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The magnetism and spin dynamics of $[Cr_4S(O_2CCH_3)_8(H_2O)_4](NO_3)_2 \cdot H_2O$ have been investigated by magnetic susceptibility and proton NMR measurements and by theoretical calculations. The proton-spin lattice relaxation rate $1/T_1$, as a function of the temperature T and external magnetic field B, provides a very useful probe of the dynamical behavior of the four Cr^{+3} (spins $s=\frac{3}{2}$) paramagnetic ions which are ferromagnetically coupled via isotropic Heisenberg exchange interaction. From our derived formulas for the two-ion time correlation functions, we find that $1/T_1$ may be expressed as a function of the single scaling variable $\mu_B B/(k_B T)$, where μ_B is the Bohr magneton and k_B is Boltzmann's constant, for the regime of our measurements. Our experimental data are in good agreement with this prediction and our derived form of the scaling function.

The great progress[1–4] made in recent years in synthesizing bulk samples of identical molecular-size magnetic complexes containing relatively small numbers of mutually interacting paramagnetic ions (''spins'') has provided the opportunity to systematically investigate magnetism at the mesoscopic scale. It is noteworthy that the intercomplex interactions between spins are in many cases negligible over the temperature range of typical measurements compared to those within a given complex. This property greatly simplifies the analysis since the magnetic properties of a bulk sample are determined in such cases by intracomplex spin-spin interactions alone. However, the diversity in the practical choices of spins and their placement within a complex is matched by the great diversity of their properties. In many cases the Heisenberg model of isotropic exchange interaction between the spins of a given complex provides a satisfactory theoretical framework.

In this paper we summarize the major results of our combined experimental and theoretical study of a magnetic cluster compound, $[Cr_4S(O_2CCH_3)_8(H_2O)_4](NO_3)_2 \cdot H_2O$, to be abbreviated as Cr_4-NO_3, which may be pictured as four Cr^{+3} ions (individual spins $s=\frac{3}{2}$) situated at the vertices of a nearly regular tetrahedron that is embedded within the host complex. The primary motivation of this work is to elucidate the spin dynamics of a cluster compound that is amenable to a comprehensive theoretical as well as experimental study. The understanding derived from a study of a benchmark material such as this may further the understanding of other diverse magnetic complexes. It should be noted that the present compound differs from one investigated previously,[5] to be abbreviated as Cr_4-BF_4, which featured a BF_4 radical rather than the NO_3. The crystal structure and dimensions of the two compounds are essentially identical.

We have measured the magnetic susceptibility and the proton spin-lattice relaxation rate $1/T_1$ of Cr_4-NO_3. Using our susceptibility data we determine the strength of the exchange interaction between Cr ions as well as the value of the total spin S of the ground state. We find that our $1/T_1$ data are in good agreement with the predictions of our theory briefly described below which is based on a first-principles quantum-mechanical calculation of the equilibrium two-spin time correlation functions for the Heisenberg Hamiltonian of Eq. (1). In addition to providing information on the low-frequency portion of the dynamics of the interacting spins, that can be accessed by measuring $1/T_1$ using NMR techniques, the time correlation functions are invaluable for giving detailed predictions for eventual inelastic neutron-scattering measurements. For the regime of temperatures ($1.5<T<30$ K) and external magnetic fields ($0.5<B<5.5$ T) of our measurements, we find that $1/T_1$ may be expressed as a function of a single scaling variable $\mu_B B/(k_B T)$, a prediction in good agreement with our experimental data. (Here μ_B is the Bohr magneton and k_B is Boltzmann's constant.) The scaling property is an immediate consequence of the fact that in this regime of T and B, only the $S=6$ ground-state manifold of the Heisenberg Hamiltonian is relevant. In fact, we find that $1/T_1$ is proportional to $T\chi(T,B)$, where $\chi(T,B)=\partial M(T,B)/\partial B$ is the *field-dependent* differential paramagnetic susceptibility per mole of formula units (mol FU) described as independent $S=6$ spins.

We idealize the structure as four Cr ions which are situated at the vertices of a regular[6] tetrahedron and which interact with each other via isotropic Heisenberg exchange and with a uniform external magnetic field **B** whose direction defines the z axis.[7] The model Hamiltonian reads

$$H=-J\sum_{m=1}^{3}\sum_{n=m+1}^{4}\mathbf{s}_m\cdot\mathbf{s}_n+\sum_{n=1}^{4}g\mu_B B s_{nz}, \qquad (1)$$

where the individual spin operators are measured in units of $\hbar$, the exchange energy J is positive for ferromagnetic inter-

actions, and g is the spectroscopic splitting factor. The simplifying feature of this Hamiltonian is that the energy eigenvalues may be written solely in terms of the total cluster spin quantum numbers S and M_s as

$$E(S,M_s,B) = -(J/2)[S(S+1)-15] + g\mu_B B M_s . \quad (2)$$

However, because of the multiplicity of eigenstates for a given pair of values of S and M_s, the normalized energy eigenvectors, to be denoted by $|SM_sK_s\rangle$, also depend on a quantum number, $K_s = 1,2,...,G_S$ for a choice of S with multiplicity G_S. For the present system the values of G_S are 4, 9, 11, 10, 6, 3, 1 for $S = 0,1,...,6$, respectively.[5] The partition function per FU is thus given by

$$Z(T,B) = \sum_{S=0}^{6} G_s \sum_{M_S=-S}^{S} e^{-\beta E(S,M_s,B)}, \quad (3)$$

and from it one can immediately derive $\chi(T,B)$, and other standard thermodynamic quantities. As usual $\beta = 1/(k_B T)$.

To compare with our susceptibility data, obtained for $B = 10^{-2}$ T, it suffices to consider the limiting, zero-field differential paramagnetic susceptibility $\chi(T,B\to 0)$, to be abbreviated by $\chi_0(T)$. The observed susceptibility $\chi_{\rm obs}(T)$ is then well described by the expression $\chi_{\rm obs}(T) = \chi_0(T) + \chi_D$, where the calculated[8] core diamagnetism is $\chi_D = -4.078\times 10^{-4}$ cm^3/(mol FU.) However, in order to estimate the role of intercluster interactions, which have been excluded from Eqs. (1)–(3), we generalize the expression for $\chi_0(T)$ which follows from Eq. (3) to include a Weiss correction temperature Θ, so that

$$\chi_0(T) = \frac{N_A(g\mu_B)^2}{3k_B(T-\Theta)Z(T,0)} \sum_{S=0}^{6} G_S S(S+1)(2S+1) e^{-\beta E_S}, \quad (4)$$

where N_A is Avogadro's number, $E_S \equiv E(S,M_S,0)$, and $Z(T,0)$ is given by Eq. (3) with $B = 0$.

Details of the sample preparation procedures we used will be described elsewhere.[9] Our measurements of $\chi_{\rm obs}(T)$ were made using a superconducting quantum interference device magnetometer in the temperature range 1.8–300 K with $B = 10^{-2}$ T. The open squares in Fig. 1 are the values of $T[\chi_{\rm obs}(T) - \chi_D]$ versus T. The solid curve shown describes $T\chi_0(T)$ as obtained by using the theoretical expression of Eq. (4), adopting the value $g = 2$, and choosing $J/k_B = 28.0$ K and $\Theta = -0.35$ K, which yield the best fit to our data for $T[\chi_{\rm obs}(T) - \chi_D]$. These choices of parameters are very close to those obtained in Ref. 5 for $Cr_4 - BF_4$, namely $J/k_B = 29.0$ K and $\Theta = -0.4$ K. The most noteworthy conclusions to the rather good fit for all temperatures are: The simple Hamiltonian of Eq. (1) provides an adequate description, and in particular there is no basis for invoking a molecular anisotropy term DS_z^2, which is of importance in cases of macroscopic quantum tunneling;[10] because of the positive sign of J the ground state of a cluster has total spin $S = 6$; the small negative value of Θ is evidence of a very weak residual antiferromagnetic intercluster exchange interaction.

Proton NMR measurements were performed using a phase-coherent spin-echo spectrometer in the temperature range 1.5–30 K. At low temperatures the NMR spectra could

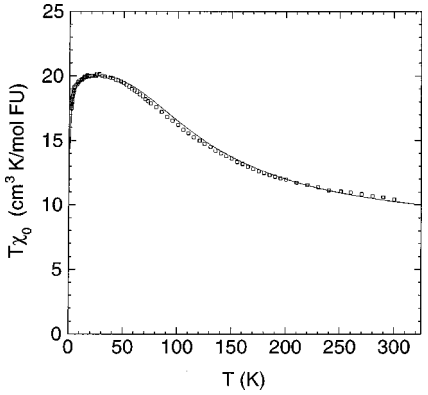

FIG. 1. Temperature dependence of $T[\chi_{\rm obs}(T) - \chi_D]$ (open squares) measured at $B = 10^{-2}$ T and the theoretical quantity $T\chi_0$ (solid curve) per mol FU in Cr_4-NO_3. The theoretical curve was calculated using Eq. (4), where the numerical values (see text) of the parameters J/k_B and Θ were chosen so as to provide the best fit to the measured data shown.

be resolved into three distinct peaks, involving small shifts from the nominal proton resonance peak at the frequency $\nu_P = \omega_P/(2\pi) = 42.58\times B$ (MHz), where B is measured in tesla. For example, for $T = 5.5$ K these peaks are shifted by $\approx$ 0, 0.75, and -1.5%, respectively. The peak associated with the largest (and negative) NMR shift can be ascribed to the protons in the H_2O molecules directly bound to the Cr core.[9] These protons are expected to be especially effective in monitoring the Cr spin dynamics. The value of T_1 was obtained by monitoring the nuclear magnetization recovery following a short sequence of saturating rf pulses. We followed the common practice[11] for molecular magnets of estimating T_1 using the initial slope of the recovery curve. For $\nu_P < 50$ MHz and temperatures in the range 5–30 K, small deviations (less than 10%) from exponential recovery behavior were observed. For $T < 5$ K or for $\nu_P > 50$ MHz the deviations typically were 20% or more and those values of T_1 have a larger experimental uncertainty. In Fig. 2 we display our results for $1/T_1$ versus T for assorted values of B. We estimate that the error bars are of order 20%. The following theoretical discussion leads to a comprehensive, simple description of our data.

The proton spin-lattice relaxation rate can probe the spectral component of the two-spin (Cr-Cr) time correlation functions at the proton Larmor angular frequency ω_P. This is predicated on the assumption that the dominant mechanism

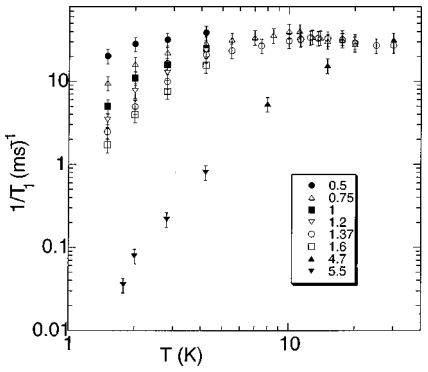

FIG. 2. Temperature dependence of the proton-spin-lattice relaxation rate T_1^{-1} for assorted values of the external magnetic field (tesla).

for proton relaxation effects is the dipolar interaction between the nuclear magnetic moments of the hydrogen atoms in the cluster with those of the four Cr ions. Specifically, $1/T_1$ is then given[12] by a linear combination of the Fourier integrals

$$\tilde{C}^{jk}_{\alpha\alpha}(\omega_P,T,B)\equiv\int_0^\infty dt C^{jk}_{\alpha\alpha}(t,T,B)\cos(\omega_P t), \tag{5}$$

where

$$C^{jk}_{\alpha\alpha}(t,T,B)\equiv\langle\delta S_{j\alpha}(t)\,\delta S_{k\alpha}(0)\rangle \tag{6}$$

is the equilibrium time correlation function for the α $(=x,y,z)$ component of the spin operators for the pair of spins j and k, $\langle\cdots\rangle=(1/Z)\mathrm{Tr}[e^{-\beta H}(\cdots)]$ denotes the canonical ensemble average, and $\delta S_{i\alpha}(t)\equiv\exp(iHt/\hbar)S_{i\alpha}\exp(-iHt/\hbar)-\langle S_{i\alpha}\rangle$. The coefficients of the linear combination of integrals, Eq. (5), are the (temperature-independent) components of the magnetic dipole interaction tensor.[12]

The evaluation of the time correlation functions of Eq. (6) is most conveniently performed by employing the complete set of eigenvectors of H, $\{|SM_SK_S\rangle\}$, as a basis. However, because of the equivalence of the four Cr spins as well as the x and y directions, there are only four distinct quantities that can arise: $C^{11}_{xx}(t,T,B)$, $C^{12}_{xx}(t,T,B)$, $C^{11}_{zz}(t,T,B)$, and $C^{12}_{zz}(t,T,B)$. For the present system there is an additional simplification that can be made. Supposing $B=0$ for a moment, and referring back to Eq. (2), the excitation energy from the Zeeman degenerate ground state $(S=6)$ to the Zeeman degenerate first excited state $(S=5)$ is $\hbar\Omega_{\mathrm{ex}}\equiv 6J\approx 168\,\mathrm{K}$. This leads to the following important practical conclusion: For the temperature range $T\leqslant 30\,\mathrm{K}$, which is the range pertinent to our experimental data for $1/T_1$, the ensemble averages can be very well approximated by restricting the trace operation[13] to the 13 eigenstates $|6,M_6,K_6=1\rangle$. This conclusion remains valid even when we consider the effects of the magnetic fields (<5.5 T) used in our NMR measurements.

A detailed analysis of the relevant matrix elements shows that the only terms contributing to the time correlation functions of Eq. (6) have a time dependence of the form $\exp(\pm i\Omega t)$, where $\Omega=0$, ω_e, Ω_{ex}, $\Omega_{\mathrm{ex}}\pm\omega_e$, and $\omega_e\,(\mathrm{GHz})=176\times B$ is the electron Larmor angular frequency for the given field. Hence the only nonzero contributions to the Fourier integrals (5) are terms that are proportional to Dirac delta functions $\delta(\omega_P-\Omega)$ for the above choices of Ω. However, since all of these choices of Ω, except[14] that of $\Omega=0$, extend far beyond the practical range of values of ω_P, it is clear that the corresponding terms of the time correlation functions play no role for $1/T_1$. By contrast, for neutron scattering, all of the above values of Ω are expected to be relevant even in this low-temperature interval, $T\leqslant 30\,\mathrm{K}$.

Now it turns out that only $C^{11}_{zz}(t,T,B)$ and $C^{12}_{zz}(t,T,B)$ contribute to the coefficient of $\delta(\omega_P)$, and they contribute equally. We find that this coefficient is, apart from a constant numerical prefactor, given by $\langle(\delta S_z)^2\rangle$, where $\delta S_z=S_z-\langle S_z\rangle$, and S_z is the operator for the z component of the total cluster spin operator. It thus follows that $1/T_1$ is proportional to the field-dependent differential susceptibility of an isolated $S=6$ particle, i.e.,

$$1/T_1(T,B)\propto T\partial\langle S_z\rangle/\partial B\propto dB_6(6x)/dx, \tag{7}$$

where B_6 denotes the Brillouin function for $S=6$, and $x\equiv g\mu_B B/(k_B T)$. Note in particular that $1/T_1$, rather than depending separately on both T and B, is a function of the single dimensionless variable x. Shown in Fig. 3 is the right-hand side of Eq. (7) as a function of x (solid curve, with only one adjustable proportionality constant) as well as our T_1 data of Fig. 2. Indeed, when plotted in this manner the data points are consistent with both a scaling description as well as the specific functional form, Eq. (7), that we have derived from our first-principles treatment of the time correlation functions. It is noteworthy that the relaxation process for this material may be described so simply, solely in terms of the fluctuations of an isolated $S=6$ particle. Moreover, the good agreement between theory and experiment suggests that lifetime effects and intercluster interactions, which have been excluded from the outset from our theoretical treatment based on Eq. (1), are either very small in this cluster compound or are very weakly dependent on T and B. The impact of these effects on $1/T_1$ has recently[15] been observed for the Cu_6 system.

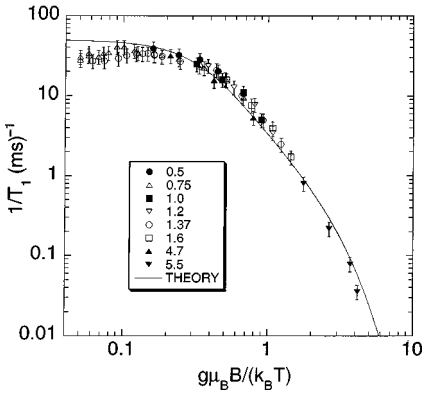

FIG. 3. Proton-spin lattice relaxation rate T_1^{-1} as a function of the scaling variable $g\mu_B B/(k_B T)$, with $g=2$, for assorted values of the external magnetic field (tesla). The solid curve is our formula (7) with an adjustable proportionality constant chosen so as to provide the best fit to the measured data.

In summary, in this paper we have provided a comprehensive description of the magnetic susceptibility and the low-frequency spin dynamics of the cluster compound Cr_4-NO_3 based on the Heisenberg model Hamiltonian, Eq. (1), for localized spins. Our key result is that we find good agreement between our data for $1/T_1$ and our derived result that this quantity is given by the specific function of the single, scaling variable $\mu_B B/(k_B T)$, listed in Eq. (7).

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[6] In reality the four Cr-Cr spacings are not strictly equal but they all lie in the range 3.72–3.91 Å (see Ref. 5).
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[13] To correctly evaluate the set of matrix elements $\langle 6M_6 1|\delta S_{i\alpha}(t)\delta S_{j\alpha}(0)|6M_6 1\rangle$ it is necessary to introduce the complete, unrestricted basis $\{|SM_S K_S\rangle\}$ of eigenstates of H.
[14] We implicitly assume that the integrals (5) should be evaluated with ω_P determined by a local magnetic field at a proton site, not only the external field. We anticipate that the local field is described by a probability distribution, perhaps Gaussian, of width of several tesla. Hence the angular frequency $\Omega=0$, and it alone, is of importance.
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